A new silage aid, process for preparing this silage aid and use of this silage aid

This invention relates to a new silage aid, process for preparation of this silage aid and use of the silage aid.

When preparing silage from for instance fish waste, the raw material is treated with acid to obtain the optimum pH (3.5-4.5) with regard to enzymatic hydrolysis, and to prevent the growth of bacteria during storage.

During the silage process hydrolysis results in the formation of emulsions made up of an acidic water phase, an oil phase and solids. The degree of phase separation in these systems depends upon the type of raw material used. Oxygen is easily transferred through water, which unfortunately gives rise to oxidative degradation of the oil phase. This lipid oxidation results, of course, in a reduced nutritional value of the oil as an ingredient both for feed and for food. Likewise, it implies a reduced quality of the oleochemicals made from fish silage oil. To overcome these problems it would be a great advantage if an antioxidant well suited for the protection of fish oil could be present during the silage process.

The most favourable way to include an antioxidant would be as a constituent of the silage aid. Generally, it would be necessary to have at least 1% antioxidant in the silage aid. Water soluble antioxidants are easily included in an acidic silage aid. Unfortunately though, these compounds will not be able to protect the oil after separation since they will not be associated with the oil phase. Furthermore, the antioxidants that are food approved in Europe and/or the US at present, are mainly fat soluble compounds, *e.g.* 2,6-di-*tert*-butyl-4-methylphenol(BHT), 3-*tert*-butyl-4-hydroxyanisole(BHA), *tert*-butylhydroquinone(TBHQ), tocopherol and the gallates. All of these food approved antioxidants are also commercially available in formulations with emulsifying agents, but unfortunately the emulsifying agents are in general hydrophobic, and thus these formulations are not well suited to an acidic water medium.

The antioxidant ethoxyquin is an exception with regard to the properties described above. Ethoxyquin is a secondary, cyclic amine. Hence, it is well known that ethoxyquin is soluble in acids at low pH (<3), as this implies protonation of the amino group and thereby formation of a hydrophilic salt. As pH rises to 4-5 however, ethoxyquin will be deprotonated and consequently, will again become fat soluble. Thus, by choosing the proper

concentration of acid it is possible to have ethoxyquin in the form of a hydrophilie salt in the silage aid. while during the silage process the salt is deprotonated. becomes fat soluble and consequently will be able to protect the oil against lipid oxidation. Likewise. other antioxidants with an amino group may be suitable for this use. The preparation of ethoxyquin formiate salt. and this salt dissolved in formic acid is disclosed in Norwegian patent application no. 851007.

Unfortunately though. ethoxyquin or other known antioxidants with an amino group. are not food approved. Therefore. when food approval has been required. no silage aid soluble antioxidants have been available to date.

Thus it is a main object of the present invention to provide a new silage aid comprising a food approved antioxidant.

This and other objects of the invention is achieved by the attached claims.

The invention will be further explained below.

The antioxidants BHT. BHA. tocopherol. TBHQ and propyl gallate(PG) are practically insoluble in water. and experiments have shown that their solubility in mineral acids (hydrogen chloride. sulphuric acid) is also quite low (see Table 1). Unexpectedly however. we have now found that these highly hydrophobic antioxidants are soluble in the short chain carboxylic acids formic. acetic and propionic acid (see Table 1). Further experiments have shown that when using a silage aid comprising BHA. TBHQ or PG dissolved in 85% formic acid. a superior quality of the fish oil product as compared to the product of the same process using only 85% formic acid (Table 2) is obtained. When the silage aid containing antioxidant is blended with the fish waste raw material. the hydrophobic antioxidant is associated with and protects the oil phase. Thus. we have found a method which is convenient on a technical scale and which leads to superior quality of the products of the silage process.

Generally. the amount of silage aid needed will depend upon the type of fish waste used and the choice of acid. Also. the amount of antioxidant needed. may depend upon the raw

material used or the requirements regarding the stability of the isolated oil. This implies that the required amount of antioxidant dissolved in the acid may vary.

Furthermore, we have shown by experiments that the solubility of BHT in formic acid increases when BHA is present in the acid. This was a surprising result.

The silage aid might further comprise additives like, anti-microbiell compounds (e.g. ethyl benzoate or benzoic acid), anti-fungal compounds, anti-corrosive compounds, chelating compounds (e.g. citric acid), compounds improving the handling properties (e.g. glycerol), and oxygen scavengers.

The present invention also comprises to firstly dissolve the said antioxidants in a short chain carboxylic acid, and subsequently adding a mineral acid in the purpose of decreasing pH.

The short chain carboxylic acids according to this invention might be used either alone or in combination with their corresponding salts. Further, the aforementioned acids might be used as a mixture or as a mixture together with any of their salts.

The present invention is documented by experiments performed for a fish silage process. This invention will of course also prevail for other processes where acidic preservation is used. Fish silage shall only be considered as an example. The invention is applicable in acidic preservation of other organic by-products like slaughter waste, poultry waste and food waste, as well.

Table 1. Solubility (weight %) of antioxidants in different acids.

	BHA	TBHQ	PG	BHT	Toco-pherol
5 M hydrogen chloride[a]	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%
4 N sulphuric acid[a]	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%
85% formic acid[b]	>5%	>5%	>10%	< 0.25%	< 0.5%
98-100% formic acid[b]	>10%	>10%	>10%	< 0.25%[c]	< 0.5%
100% acetic acid[b]	>10%	>10%	>10%	>10%	>10%
100% propionic acid[b]	>10%	>10%	<10%	>10%	>10%

a)A mixture of antioxidant(40mg) and mineral acid(40g) was thoroughly shaken at 23°C. b)A mixture of the chosen amount of antioxidant(10-400mg) and acid(4g) was thoroughly shaken at 23°C. c)0.25% BHT is not soluble in formic acid. When 0.5% BHA is added to the formic acid, BHT is soluble.

Example I: Experimental procedure for a lab-scale fish silage process.

The raw material, Atlantic salmon viscera, was ground in a kitchen grinder, and the resulting minced fish waste was thoroughly blended before it was portioned into separate batches each containing 500 gram. Silage aid (2% vol./wt.; 10mL) 85% formic acid with or without 0.75% wt./vol. of dissolved antioxidant was added, and the content of each batch was mixed to ensure a homogenous distribution. The batches was stored for eight days in an oven at 35±2°C, before a standard procedure for silage work up was conducted. This included warming the silage at 90±1°C for 1 minute, tempering, and finally separating the oil after centrifugation. The isolated oils were analysed to determine the POV and *p*-AV. Furthermore, weight gain (at 35±1°C) as a function of time was registered to determine the IP of the oils. The results are presented in Table 2.

Example II: Experimental procedure as in Example I, but the raw material in this series was whole herring. The results are presented in Table 2.

Table 2. Comparison of the results from analysis of various oil quality parameters[a], determined for fish silage oil produced[b] using silage aid with or without dissolved antioxidant.

Example no.	Silage aid[c]	POV	*p*-AV	IP
I	Control: 85% HCOOH (formic acid)	3	24	1
	85% HCOOH incl. **BHA** (150ppm)	2	22	19
	85% HCOOH incl. **TBHQ** (150ppm)	1	9	62
II	Control: 85% HCOOH	29	29	0
	85% HCOOH incl. **PG** (150ppm)	7	19	4

a)POV(Peroxide value, Ph. Eur. V.3.4.5); determines the amount of primary oxidation products, hydroperoxides, in the oil. *p*-AV(*p*-Anisidine value, IUPAC 2.504); determines

the amount of some secondary oxidation products. alkenals. in the oil. IP(induction period); a measure of the shelf life of the oil. given as the number of days it takes before the oil shows detectable weight gain due to oxygen absorption. b)The experimental procedure for lab-scale silage experiments is given above in example I. c)The concentration of antioxidant given in parenthesis. is based on the amount of fish waste used in these experiments.